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(54) PREPARATION OF HOP EXTRACT

(71) We, PFIZER INC., formerly known as Chas. Pfizer & Co., Inc., a Corporation organized under the laws of the State of Delaware, United States of America, of 235, East 42nd Street, New York 17, State of New York, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

Beer and ale and similar malt beverages are produced from water, barley malt, adjuncts and hops. The malt and adjuncts furnish the carbohydrates and other growth essentials which make up the wort. This wort, boiled with hops, in turn forms the basic substance for fermentation in the fermenting tanks. The hops give the characteristic bitter flavor and pleasant aroma to the beer.

The commercially available extracts of hops are prepared by extracting and refining the resins and oils obtained from natural hops. These extracts are prepared either with pre-isomerized or with non-isomerized humulones. The preparation of non-isomerized hope extracts is disclosed in United States Specification No. 2,952,546 and in United States Specification No. 3,092,497. These compositions must be added to wort during kettle boiling so that the humulones may be isomerized to isohumulones.

A process for preparing a pre-isomerized hop concentrate is disclosed in United States Specification No. 3,155,522. The concentrated converted active constituents may be added to the wort during the manufacture of a brewed beverage or to the brewed beverage.

A process for preparing a pre-isomerised hop extract is disclosed in United States Specification No. 3,044,879, and consists of extracting the bittering components of the hops, chemically isomerizing the humulones and reducing the isohumulones by means of a metal borohydride. The resulting extract which retains the bitterness and flavor of the hops is added at the wort stage. Beer made with this extract is less subject to deterioration due to light than are beers made with natural hops or unreduced hop extracts.

The reduced isohumulones contained in the hope extract prepared by the process of United States Specification No. 3,044,879 are present in the relatively insoluble free acid form, and the extract is not suitable for addition to ruh (the rest period after the wort is fermented with yeast) or to the primary filtered or finished beer because it does not readily disperse or dissolve.

The primary object of this invention is to provide a completely water-soluble pre-isomerized reduced hop extract that can be added to wort during the brewing process, any of the post-fermentation stages, or most importantly, to beer just before the final filtration step. Bottled beer prepared with reduced isohumulones is stable to the deleterious effects of light.

The present invention embodies a process whereby a hop extract is prepared by isomerizing with alkali and reducing with borohydride a hexane extract of hops and converting the reduced isohumulones to the potassium salts. This water-soluble extract retains the bitterness and flavour of hops, and possesses the additional important advantages that it can be added to wort during the brewing process, to any of the post-fermentation stages or to beer before the final filtration step.

This invention relates to the preparation of water-soluble reduced isohumulones obtained from hops. More specifically, it is concerned with the potassium salts of these reduced isohumulones.

According to the present invention there is provided in a process for preparing a hop extract by extracting the humulones from said hops with hexane, concomitantly isomerizing and reducing said humulones by heating in the present of sodium borohydride solution containing sodium hydroxide, acidify-

ing the reaction solution and extracting said reduced isohumulones with hexane, the improvement which comprises converting said reduced isohumulones to water-soluble potassium salts by mixing said hexane extract with fresh water, heating to a temperature between 50°C. and 60°C., adjusting the hot hexane-water mixture to pH 7.5 to 9.0 with aqueous potassium hydroxide and separating the aqueous phase containing said potassium salts of reduced isohumulones.

Hops contain hard and soft resins, oils, wax, substances soluble in water such as tannins, proteins and pectins, and a certain amount of cellulose matter. The soft resins consist of humulones and lupulones.

The expression "humulone" is here used as a generic term to include the α-acids present in hops. The soluble salts of these humulones are here called "humulates". "Isohumulones" are humulones that are isomerized by heating aqueous solutions of humulates. The expression "lupulones" used here means the weak β-acids of hops, and "lupulates" are the corresponding water-soluble salts.

Humulones and other resins including lupulones are extracted from dried and crushed hops with several portions of hexane at reflux temperature until the extraction of hop resins is substantially complete. The combined solvent extract are filtered and concentrated under vacuum to a hexane concentrate containing about 35—45% dissolved solids.

The humulones can be isomerized by heating an aqueous solution of the sodium or potassium humulates. Subsequent reduction can be accomplished by reacting the sodium or potassium isohumulates with sodium or potassium borohydride. In the practice of this invention, the isomerization and reduction processes are combined. The concentrated hexane hop extract is added to an aqueous solution of sodium borohydride containing sodium hydroxide, and heated for about 2 to 4 hours at 55—62°C. (preferably at 60—62°C., the reflux temperature range of the contained hexane). After isomerization and reduction, quantitative determination of reduced isohumulones is made by spectrophotometric assay.

After the completion of the isomerization and concomitant reduction, the reaction mixture is cooled to between 50 and 60°C. (at temperatures below 50°C. a layer of tarry hop resins comes out of solution), and acidified to about pH 1—2 with an aqueous solution of sulphuric acid containing ammonium sulfate. The ammonium sulfate, by increasing the specific gravity of the aqueous solution, facilitates the separation of the hexane and aqueous phases. The reduced isohumulones which are in the free acid form are extracted in the hexane phase. The aqueous phase, maintained at 50—60°C., is re-extracted with a portion of fresh hexane. Inorganic salts and boric acid derived from the borohydride reduction remain in the aqueous phase which is discarded. The hexane extracts are combined, washed with water and concentrated under vacuum.

The reduced isohumulones can be extracted from the solvent phase by mixing with water and adding alkali to convert the compounds to water-soluble reduced isohumulates. The alkali must be used in sufficient quantity to produce a final pH which extracts all the reduced isohumulones in the form of reduced isohumulates, but preferably insufficient to extract the undesirable lupulones in the form of lupulates. Sodium of potassium carbonate may be used but have the disadvantage that for every mole of carbonate added, a mole of bicarbonate is formed. The added concentration of sodium or potassium bicarbonate has a salting-out effect on the reduced isohumulates and limits the final desired aqueous concentration.

In the practice of this invention, the hexane concentrate containing the reduced isohumulones is mixed with a portion of fresh water, and heated to a temperature of 50—60°C., a temperature range sufficient to keep the hope components in solution without, at the same time, allowing excessive volatility losses of hexane. The pH of the hot hexane-water mixture is carefully adjusted with alkali to 7.5 to 9.0. Potassium hydroxide or sodium hydroxide may be used but potassium hydroxide is preferred because of the greater stability of the solution of the potassium salts of the reduced isohumulones. The pH range of 7.5 to 9.0 is critical in that maximum aqueous solubility of the potassium reduced isohumulates is achieved above pH 7.5 while limiting the aqueous extraction of lupulones as potassium lupulates formed at a pH higher than 9.0.

The phases are allowed to separate while hot, and the aqueous phase containing the potassium salts of reduced isohumulones is removed from the hexane phase which contains lupulones, hop oils and waxes, and is discarded. The aqueous solution is filtered and concentrated under vacuum to yield an aqueous concentrate containing about 30—60% dissolved solids.

The following example is provided to illustrate the present invention, but not to limit its scope.

Example

A 212 gram portion of dried ground hops is extracted with 3 liters of refluxing hexane (64°C.) in a flask. The extract is removed and the hops are extracted twice more in the same manner with fresh hexane. The extracts are filtered and concentrated under vacuum to a concentrate containing about

40% dissolved solids and 60% hexane. The 72 grams of concentrate contains 14.4 grams of humulones and 7.2 grams of lupulones by spectrophotometric assay.

9.85 grams of 12% sodium borohydride solution containing 40% sodium hydroxide is added to 154 ml. of water and heated to about 60°C. The concentrated hop extract is added and the solution refluxed for 3 hours (60—62°C.) to isomerize and reduce the humulones. The reaction mixture is cooled to about 50—60°C. and acidified to about pH 1.6 with an aqueous solution containing 10.3 grams of sulfuric acid and 11.1 grams of ammonium sulfate. The phases are separated while hot and the aqueous layer is re-extracted with 90 ml. of fresh hexane at 50—60°C. The hexane layers are combined and washed with about 60 ml. of water at 50—60°C. The aqueous wash is re-extracted with 50 ml. of fresh hexane at 50—60°C. The combined hexane extracts are concentrated under vacuum to yield a hexane solution containing 17.2 grams of reduced isohumulones and approximately 5.0 grams of lupulones.

The hexane solution of reduced isohumulones is mixed with about 170 ml. of water in a flask and heated to between 50 and 60°C. The pH of the hot mixture is adjusted to 7.5 to 9.0 with 4.65 *N* KOH. The phases are separated while hot and the hexane phase is re-extracted with about 80 ml. of water at pH 7.5—9.0 at a temperature of about 50 to 60°C. The aqueous layers are combined, filtered at room temperature and then concentrated under vacuum. The concentrated solution contains 13.4 grams of reduced isohumulone potassium salts and 0.7 grams of lupulones.

WHAT WE CLAIM IS:—

1. In a process for preparing a hop extract by extracting the humulones from said hops with hexane, concomitantly isomerizing and reducing said humulones by heating in the presence of sodium borohydride solution containing sodium hydroxide, acidifying the reaction solution and extracting said reduced isohumulones with hexane, the improvement which comprises converting said reduced isohumulones to water-soluble potassium salts by mixing said hexane extract with fresh water, heating to a temperature between 50°C. and 60°C., adjusting the hot hexane-water mixture to pH 7.5 to 9.0 with aqueous potassium hydroxide and separating the aqueous phase containing said potassium salts of reduced isohumulones.

2. Potassium salts or reduced isohumulones whenever prepared by the process of claim 1.

3. An improved process for preparing a hop extract substantially as described herein.

4. A hop extract whenever prepared by the process substantially as described herein.

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